Supporting Information

Aluminum-Ion-Intercalation Nickel Oxide Thin Films for High Performance Electrochromic Energy Storage Devices

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Table S1. The X-ray diffraction patterns of the NiO (111) and (200) peak.

	As-deposited		200 ℃		300 ℃		400 ℃	
	(111)	(200)	(111)	(200)	(111)	(200)	(111)	(200)
2θ (degree)	37.73	43.85	37.66	43.69	37.41	43.45	37.37	43.41
TC	0.12	0.88	0.09	0.91	0.22	0.78	0.14	0.86

Table S2. The thickness, refractive index and packing density of NiO films at different annealing temperatures.

Annealing temperature (℃)	Thickness (nm)	Index of films	Packing density
As-deposited	498.8	1.65	0.61
200	521.0	1.72	0.66
300	441.5	1.73	0.67
400	522.6	1.80	0.72

Table S3. The roughness of NiO films at different annealing temperatures.

Annealing temperature (℃)	R_a (nm)	R_q (nm)
As-deposited	3.07	3.88
200	4.22	5.29
300	3.61	4.53
400	5.09	6.36

Table S4. Calculated parameters using the EIS technique for all of the synthesized samples.

	As-deposited		200 ℃		300 ℃		400 ℃	
	0 V	1.2 V	0 V	1.2 V	0 V	1.2 V	0 V	1.2 V
R_s (Ω cm^{-2})	7.59	6.08	9.60	9.15	9.87	9.51	7.86	7.58
R_{ct} (Ω cm^{-2})	64.81	141.51	76.25	7.59	17.22	2.83	9.27	7.86
C_{dl} (F cm^{-2})	1.09e-05	1.56e-04	1.56e-05	1.72e-05	3.56e-04	7.46e-06	5.90e-10	7.02e-10

Table S5. Detail data of *ex situ* XPS results.

	Initial state		0 V		1.2 V	
	Ni^{2+}	Ni^{3+}	Ni^{2+}	Ni^{3+}	Ni^{2+}	Ni^{3+}
Position (eV)	851.3	853.2	853.9	855.8	854.4	856.0
Area (%)	41.6	58.4	43.2	56.8	24.6	75.4
FWHM	1.40	2.44	1.37	2.27	1.04	3.24

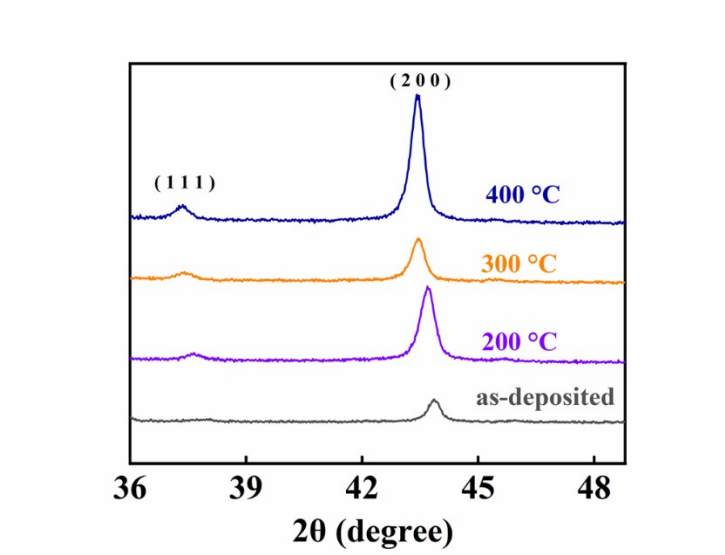
Table S6. Detail data of O_{1s} XPS results.

	Initial state		0 V			1.2 V		
	NiO	Ni_2O_3	NiO	Ni_2O_3	-Al-O-Al-	NiO	Ni_2O_3	-Al-O-Al-
Position (eV)	526.9	528.4	529.6	531.2	532.7	529.7	531.4	532.7
Area (%)	38.7	61.3	27.8	41.8	30.4	29.0	66.5	4.50
FWHM	0.941	2.47	1.12	2.53	1.55	1.09	3.10	0.875

Table S7. Calculated for the specific capacitance (C), the energy density (E) and power density (P) at various current density.

Current density (mA cm^{-2})	0.04	0.08	0.12	0.16	0.20	0.24
C (F g^{-1})	9.97	7.63	6.85	6.07	5.72	5.52
E (Wh kg^{-1})	12.5	9.53	8.56	7.58	7.15	6.90
P (W kg^{-1})	218	436	654	872	1090	1308

S1. XRD patterns of the NiO (100) peak and (200) peak.



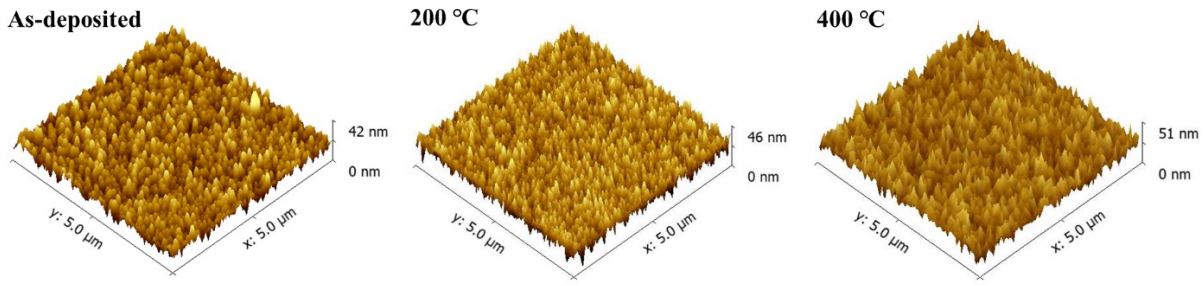
S2. Packing density (P, **Fig. 1b**)

The packing density (P) is calculated based on the formula:[1, 2]

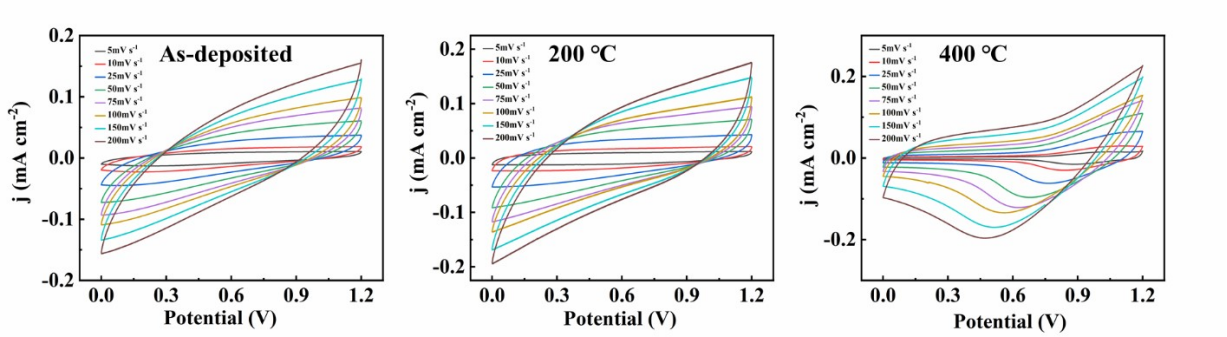
$$P = \left(\frac{{n_f}^2 - 1}{{n_f}^2 + 2}\right)\left(\frac{{n_b}^2 + 2}{{n_b}^2 - 1}\right) \quad (1)$$

where n_f and n_b represent the refractive index of films and bulk NiO (n_b=2.33 at 633 nm^3), respectively.

S3. AFM images for NiO thin films at various annealing temperatures.



S4. Cyclic voltammograms for the NiO thin films from 5 to 200 mV/s.



S5. Computational Methods.

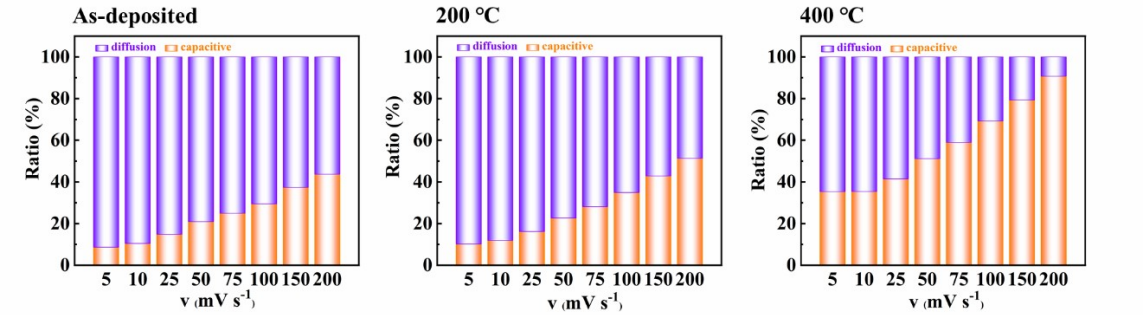
Regarding the adsorption behavior of Al atoms at different sites on the NiO (111) surface, 6 layers of 3×3×1 supercells are constructed on the NiO (111) plane under 15 Å vacuum. The deepest four layers are fixed, while the first two layers are completely relaxed. The structural optimization is set to 2×2×1 by the Monkhorst-Pack[4] scheme, and the density of states (DOS) is set to 5×5×1. In order to clarify the interaction between the NiO surface and the adsorbed Al atom, van der Waals corrections are performed using the DFT-D3 method.[5, 6] The adsorption energy is calculated by the following equation:

$$E_{ads} = E_{NiO/Al} - E_{NiO} - E_{Al} \quad (2)$$

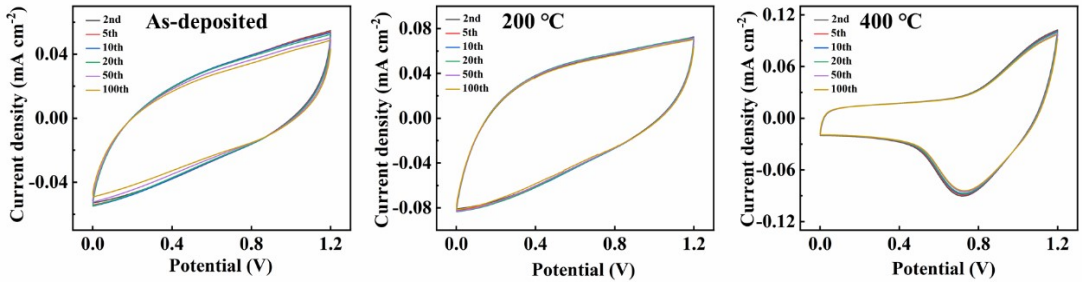
where $E_{NiO/Al}$, E_{NiO} and E_{Al} are the total energy of the slab model covered by Al atoms, the isolated adsorbate NiO (111) plane and the total energy of each atom for the bulk

Al, respectively.

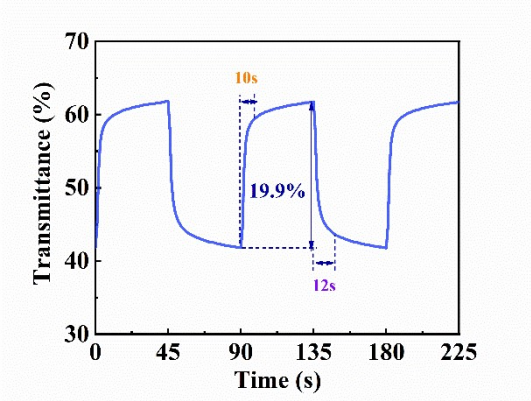
S6. Separation of contributions from capacitive and diffusion-controlled process as a function of processes at different scan rates for the NiO thin films at various annealing temperatures.



S7. Cyclic voltammograms for the NiO thin films at 50 mV/s scan rate at various annealing temperatures.



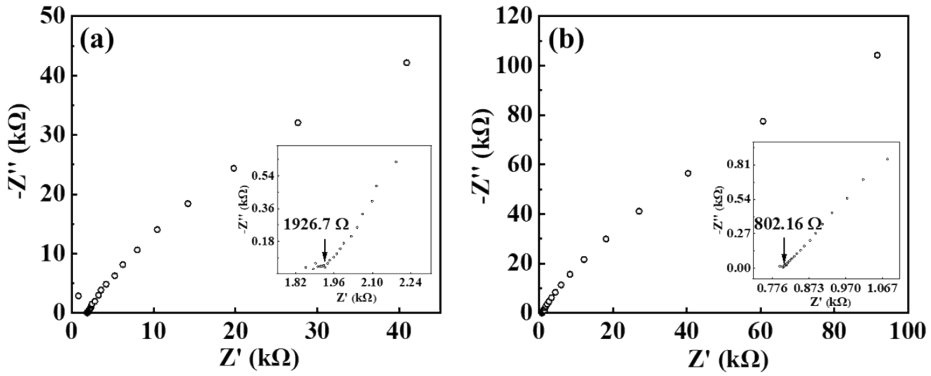
S8. The *in situ* optical transmittance spectra of the NiO thin films annealed at 300°C.



S9. Nyquist plots for the (a) $LiClO_4$-PC electrolyte and (b) $Al(ClO_4)_3$-PC electrolyte (the insets show the magnified high-frequency region of the Nyquist plot). The ionic conductivity (σ, mS cm^{-1}) of the electrolytes is calculated by the equation:

$$\sigma = \frac{L}{RA} \tag{3}$$

where L(cm) and A(cm^2) is the distance and electrode surface area of the two glassy carbon electrodes, respectively. In the high-frequency region, the real axis (x intercept) represents the resistance (R). The ionic conductivity of the Al^{3+}-containing electrolyte (0.1 M) is calculated to be 22.9 mS cm^{-1}, larger than that (9.55 mS cm^{-1}) of the Li^+-containing electrolyte (0.1 M).



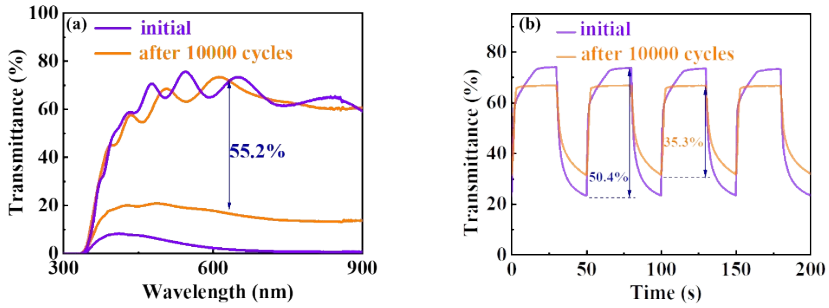
S10. The power density and energy density are two key parameters to evaluate the energy storage performance of supercapacitors. The energy density (E) and power density (P) can be calculated by equation (4) and equation (5):

$$E = \frac{\frac{1}{2}C\Delta v^2}{3.6} \tag{4}$$

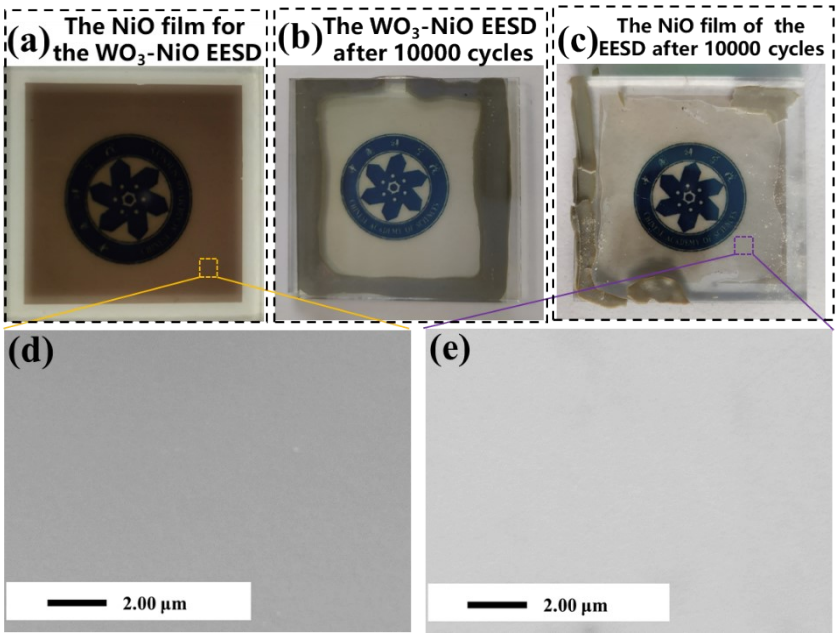
$$P = \frac{3600E}{\Delta t} \tag{5}$$

where E (Wh kg^{-1}), P (W kg^{-1}), C (F g^{-1}), ΔV (V), Δt (s) are the energy density, the power density, the specific capacitance, the range of the potential from the GCD curves, and the total discharge time, respectively.[7]

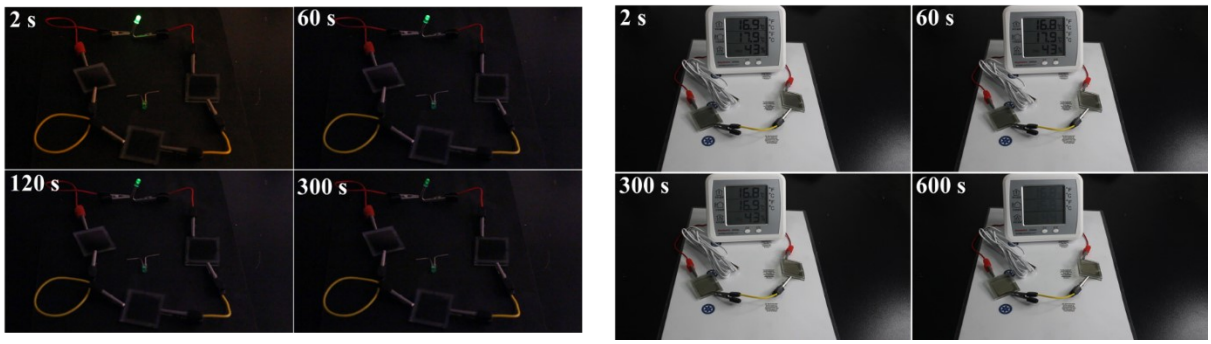
S11. (a) The transmittance spectra of the EESD in the wavelength range from 300 nm to 900 nm before and after 10000 cycles (-1.5 V/+1.5 V). (b) The transmittance spectra for the initial state and the transmittance curves after 10000 cycles at $\lambda_{633\ nm}$ (-1.3 V/+1.5 V, 50 s per cycle).



S12. Digital photos of (a) the NiO thin film before encapsulating into the WO_3-NiO EESD, (b) the WO_3-NiO EESD after 10000 cycles and (c) the NiO thin film of the WO_3-NiO EESD after 10000 cycles. (d-e) The SEM surface images corresponding to the surfaces on the NiO thin films.



S13. Digital photographs of EESDs powering LED (a) and LCD (b).



(a) **(b)**

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